

Free energy of multicomponent embryo formation

Victor Kurasov

Victor.Kurasov@pobox.spbu.ru

This publication continues description presented in [1] taking into account all definitions and facts from [1].

Due to the compact character of the embryo of the liquid phase one can consider it in the state of the internal equilibrium.

In the capillarity approximation the free energy of the embryo consists of the volume part and of the surface part. The surface part F_S has the form

$$F_S = S\gamma \ ,$$

where γ is the surface tension, S is the square of the surface. In the capillarity approximation it is supposed that the surface tension is the surface tension of the plane surface.

The volume part F_V of the free energy F has the form

$$F_V = - \sum_i b_i \nu_i \ ,$$

where ν_i are the numbers of the molecules of the different components inside the embryo, b_i are the excesses of the chemical potentials in the bulk phase calculated from the saturated case, index i has the values $1, \dots, m$ for the components in the embryo. The set $\{\nu_i\}$ of the numbers of the different components inside the embryo is the most simple set from the kinetic point of view as far as the numbers of the molecules varies separately in the elementary act of interaction.

The bulk phase is considered in the frames of the capillarity approximation as the homogeneous solution.

For F one can get

$$F = - \sum_i \nu_i b_i + S\gamma \tag{1}$$

Gibbs-Duhem equations

For b_i one can come in frames of the standard theory of solutions to the following equations

$$b_i = \ln\left(\frac{n_i}{n_{i\infty}(\xi)}\right) \ , \tag{2}$$

where there is the molecule number density of the saturated vapor of the given concentration in the denominator. The concentrations ξ_i of the component i

form the vector ξ . They satisfies to $\sum_i \xi_i = 1$. In the further considerations we shall use the definition ξ for m dimensional vector or for $m - 1$ dimensional vector without any special notations.

According to the thermodynamic definitions of the activity coefficients f_i

$$n_{i\infty}(\xi) \equiv n_{i\infty}|_{\xi_i=1} \xi_i f_i(\xi) \quad . \quad (3)$$

The parts of the chemical potential which depend on these coefficients are the regular functions in the limit situations. This property extracts the activity coefficients.

The activity coefficients satisfy the equations analogous to the Gibbs-Duhem one

$$\sum_a \xi_a d \ln(f_a) = 0 \quad (4)$$

simply due to the chosen function dependencies. This is the consequence of the expression for the differential of the free energy

$$dF_V = - \sum_i b_i d\nu_i \quad .$$

To fulfill the further considerations we have to notice the following very important fact, which will be called as the principle of the correspondence. **The Gibbs-Duhem equation has to be written in the same geometrical construction as the approximation for the free energy.** The problem of the construction of the Gibbs-Duhem equation is connected with the concrete approximation in which the free energy is written. In the capillarity approximation the surface tension is taken as the surface tension of the plane surface. This point has the principal significance. For the spherical embryo the square of the surface is connected with the number of the embryo. For the plane film the square of the surface is the independent parameter. So, in the Gibbs-Duhem equation it has to be considered as the independent one. So, the differential of the free energy can be written as

$$dF = - \sum_i b_i d\nu_i + \gamma dS \quad .$$

For the embryo as the object of the Gibbs-Duhem equation it can be written

$$- \sum_i \nu_i d \ln(f_i) + S d\gamma = 0 \quad . \quad (5)$$

From the first point of view the natural definition of the concentration is the following one

$$\xi_i = \frac{\nu_i}{\sum_j \nu_j} \quad . \quad (6)$$

Then

$$\sum_i \xi_i d \ln(f_i) - \tilde{S} d\gamma = 0 \quad , \quad (7)$$

where $\tilde{S} = S/(\sum_i \nu_i)$. As far as the first sum has to go to zero one can get

$$\tilde{S}d\gamma = 0$$

The last equation is rather naive one and is gotten with account of the Gibbs-Duhem equation for the whole embryo which doesn't satisfy to the mentioned principle of the correspondence. Certainly, it is impossible to believe that one can not differentiate the surface tension on the concentration.

The last equation is presented as far as it accumulates the phenomenological rule of Wilemski and Renninger which forbid to differentiate the surface tension in the expression for the saddle point. The connection with the geometrical aspects of the approximation has not been established earlier. Now we see that this is really the paradox and this paradox is the consequence of the approximation for the free energy.

Note that when the microscopic corrections due to the curvature are taken into account, the Gibbs-Duhem equation must be also corrected in the corresponding terms due to the changed geometry.

The physical reason for the Wilemski-Renninger paradox

The physical reason of the Wilemski-Renninger paradox is existence of the surface layer with the changed concentration. The difference of this concentration from the bulk value compensates the variations of the surface tension. In some naive model one can say that it is profitable for the molecules of some component to move to the surface layer to decrease the surface tension. Certainly, they will move until the moment of some stability when the further variation of the concentration will not lead to decrease of the surface tension, i.e. when the derivative of the surface is equal to zero. Stress again that this qualitative picture is rather naive, but it will open the way to construct the capillarity model with the surface excesses which will be done later.

The difference in the sets of the independent variables in the determination of the saddle point and in the Gibbs-Duhem equation.

Here some certain disadvantages of the mentioned model will be presented. The Gibbs-Duhem equation was derived with account that the chemical potentials are not connected with the number of the molecules of the components in the embryo. But this connection exists and can be taken into account. This account leads to the two different approaches.

Neglect this dependence, i.e. put $(\partial\nu_i/\partial\nu_j) = \delta_{ij}$, and get

$$\left(\frac{\partial F}{\partial\nu_i}\right)_{\nu_j} = -b_i + \left(\frac{2\gamma}{r}\right)v_{li} \quad , \quad (8)$$

where r is the radius of the embryo,

$$v_{li} = \left(\frac{\partial V}{\partial\nu_i}\right)$$

is the volume for one molecule in the liquid phase, V is the volume of the embryo. Then in the saddle point

$$\frac{b_a(\xi)}{v_{la}} = \frac{b_b(\xi)}{v_{lb}} \quad . \quad (9)$$

Express $(\partial\nu_i/\partial\nu_j)$ through the concentrations (due to the finite number of the molecules in the embryo) and get

$$\frac{\partial F}{\partial\nu_i} = - \sum_j b_j \frac{\partial\nu_j}{\partial\nu_i} + \gamma \frac{\partial S}{\partial\nu_i}$$

or

$$\frac{\partial F}{\partial\nu_i} = - \frac{b}{\xi_i} + \gamma \frac{2}{r} \frac{v}{\xi_i} ,$$

where

$$v = \sum_j v_l \xi_j ,$$

$$b = \sum_j \xi_j b_j .$$

One and the same equation appears for every component

$$b = \gamma \frac{2}{r} v$$

for the saddle point.

Also there appears the certain difficulty connected with the absence of the connection between the concentrations and the numbers of the molecules in the embryo (the integral definition of the concentration is only some approximation). As a result one can propose the capillarity model with the surface excesses of components

The excesses of the components

To give more justified value of the free energy one can use the formalism of the Gibbs method of the dividing surfaces. The formalism prescribes to put on the considered surface the excesses $\tilde{\nu}_i$ (consider the surface of tension) of the molecules of component i .

Then the concentration can be defined as

$$\xi_i = \frac{\nu_i - \tilde{\nu}_i}{\sum_j (\nu_j - \tilde{\nu}_j)} .$$

This leads to

$$- \sum_i \xi_i db_i + \sum_i \frac{\tilde{\nu}_i}{\sum_k (\nu_k - \tilde{\nu}_k)} db_i + \frac{S}{\sum_k (\nu_k - \tilde{\nu}_k)} d\gamma = 0$$

with the concrete realization

$$- \sum_i \xi_i \frac{db_i}{d\xi_j} + \sum_i \frac{\tilde{\nu}_i}{\sum_k (\nu_k - \tilde{\nu}_k)} \frac{db_i}{d\xi_j} + \frac{S}{\sum_k (\nu_k - \tilde{\nu}_k)} \frac{d\gamma}{d\xi_j} = 0 .$$

Due to concrete form of the activity coefficients the first term goes to zero and

$$\sum_i \frac{\tilde{\nu}_i}{\sum_k (\nu_k - \tilde{\nu}_k)} db_i + \frac{S}{\sum_k (\nu_k - \tilde{\nu}_k)} d\gamma = 0$$

with the concrete realization

$$\sum_i \frac{\tilde{\nu}_i}{\sum_k (\nu_k - \tilde{\nu}_k)} \frac{db_i}{d\xi_j} + \frac{S}{\sum_k (\nu_k - \tilde{\nu}_k)} \frac{d\gamma}{d\xi_j} = 0 \quad .$$

The last relation forms the system of $m - 1$ equations. Then all excesses are defined with one arbitrary constant. This constant can be fixed if the distance between the considered surface and the equimolecular surface is known. It is natural to consider the surface of tension as the basic surface as far as the tension is prescribed only to this surface.

On the level of the differentiates one can get

$$\sum_i (\nu_i - \tilde{\nu}_i) db_i + \sum \tilde{\nu}_i db_i - S d\gamma = 0 \quad .$$

The first sum goes to zero which leads to

$$\sum \tilde{\nu}_i db_i - S d\gamma = 0$$

or

$$\sum_i \frac{\tilde{\nu}_i}{S} db_i = d\gamma \quad .$$

The global structure of the free energy

At first we shall describe the global structure without excesses of the components of the embryo.

In terms of $b(\xi)$ then

$$F = -\nu b(\xi) + S\gamma \quad , \quad (10)$$

where

$$\nu = \sum \nu_i \quad .$$

To have the condensation it is necessary and sufficient to have the positive values of $b(\xi)$. Introduce

$$B(\xi) = \frac{b(\xi)}{6\pi^{1/2}\gamma^{3/2}v} \quad . \quad (11)$$

Suppose that the volumes for one molecule depend on the concentration weakly. Introduce

$$\kappa = (S\gamma)^{3/2} = 6\pi^{1/2}\nu\gamma^{3/2}v \quad . \quad (12)$$

Then

$$F = -\kappa B(\xi) + \kappa^{2/3} \quad . \quad (13)$$

All channels are the straight lines, they start at the origin of the coordinates of the number of the molecules in the embryo and don't cross. The independent consideration of every channel is possible.

For the characteristics of the saddle point one can get

$$\kappa_m = \left(\frac{2}{3B(\xi)}\right)^3 \quad , \quad (14)$$

$$F_m = \kappa_m^{2/3}(\xi)/3 \quad . \quad (15)$$

Global structure with excesses

Under the macroscopic description

$$\tilde{\nu}_a = \lambda_a S \quad . \quad (16)$$

Certainly,

$$\lambda_i = \lambda_i(r) \quad .$$

But the application of the Gibbs-Duhem equation for the film requires the plane surface. Then it is necessary to put

$$\lambda_i = \lambda_i(r = \infty) \quad .$$

The mentioned property is the concrete realization of the principle of the "unique curvature": **All surface characteristics and the Gibbs-Duhem equation must be referred to one and the same surface.**

Then

$$F = - \sum_i [b_i(\xi)\xi_i + b_i(\xi)\xi_i \frac{\tilde{\nu}_i}{\nu_i - \tilde{\nu}_i}] (\sum_a (\nu_a - \tilde{\nu}_a)) + S\gamma \quad . \quad (17)$$

Let the surface of tension S be the surface around all molecules inside the embryo (to be the equimolecular surface). Then

$$\sum_a (\nu_a - \tilde{\nu}_a) v_{l\ a} = \frac{S^{3/2}}{6\pi^{1/2}} \quad , \quad (18)$$

$$F = - [\sum_i \xi_i b_i(\xi) + \sum_i \frac{\tilde{\nu}_i}{\nu_i - \tilde{\nu}_i} \xi_i b_i(\xi)] \frac{\kappa}{v6\pi^{1/2}\gamma^{3/2}} + \kappa^{2/3} \quad . \quad (19)$$

It is necessary to express ν_i through $S^{3/2}$. Then

$$\frac{\tilde{\nu}_i}{\nu_i - \tilde{\nu}_i} \xi_i = \frac{v6\pi^{1/2}\gamma^{1/2}}{\kappa^{1/3}} \lambda_i \quad . \quad (20)$$

For the free energy one can approximately get

$$F = - [\sum_i \xi_i b_i(\xi)] \frac{\kappa}{v6\pi^{1/2}\gamma^{3/2}} + \kappa^{2/3} [1 - \frac{\sum_i \lambda_i b_i(\xi)}{\gamma}] \quad . \quad (21)$$

We have the same analytical structure as the already observed one after the shifts

$$\begin{aligned} \kappa^{2/3} &\rightarrow \kappa^{2/3} [1 - \frac{\sum_i \lambda_i b_i(\xi)}{\gamma}] \quad , \\ B &\rightarrow B = \frac{[\sum_i \xi_i b_i(\xi)]}{v6\pi^{1/2}\gamma^{3/2} [1 - \frac{\sum_i \lambda_i b_i(\xi)}{\gamma}]^{3/2}} \quad . \end{aligned}$$

This model satisfies all necessary requirements of the self consistency.

References

- [1] Melikhov A.A., V.B.Kurasov, F.M.Kuni, Yu.Sch.Djikaiev, Khimicheskaya fizika (Russian journal of chemical physics), -. 9, N12 (1990) , P. 34